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CHARGE DISTRIBUTION IN XENON FLUORIDES XeF_2, XeF_4, XeF_6 AND $XeOF_4$, FROM ELECTRON SPECTROSCOPY (ESCA)

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Charge Distribution in Xenon Fluorides
XeF_2, XeF_4, XeF_6 and $XeOF_4$,
from Electron Spectroscopy (ESCA)

by

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ABSTRACT

The xenon fluorides XeF_2, XeF_4 and XeF_6 and xenon oxide tetrafluoride have been subjected to electron spectroscopy (ESCA) both in the solid and gaseous phases. Chemical shifts of the XeM_V electrons indicate that each fluorine ligand withdraws at least 0.3e, from the xenon atom. The greater the charge on the xenon atom the smaller is the charge removed by each fluorine ligand. The oxygen ligand in $XeOF_4$ is almost twice as effective in removing electron density as each fluorine ligand.

The ESCA findings are consistent with Xe-F bonding involving three centre four electron molecular orbitals and with electron pair bonding of the oxygen ligand in $XeOF_4$, as in a classical semi-ionic linkage $F_4Xe^+:O^-$.

1. Introduction

The nature of the chemical bonding in xenon fluorides and other noble gas compounds has attracted much interest and some controversy has arisen.[1,2] It appears, however, that accurate *a priori* calculations relating to xenon compounds will not be forthcoming soon and that quantitative descriptions will need to be empirically based.

Although molecular orbital descriptions of the bonding in xenon compounds have been most favored and, generally have provided a satisfactory accounting of the bonding,[2a] without involving high energy outer orbitals, this approach has not been fully established. Unfortunately the simple molecular orbital theory (involving three center orbitals)[2a] which is very successful in that it explains the molecular shapes of XeF_2, XeF_4 and $XeOF_4$, predicts XeF_6 to be octahedral. Vibrational spectroscopy[3] and electron diffraction data,[4] however, indicate that XeF_6 is not octahedral. A more specific molecular orbital description is therefore called for,[5] but, it may not be able to prove, *a priori*, a ground state geometry of lower than octahedral symmetry for XeF_6.

On the other hand, electron pair repulsion theory[2b] which allots an electron pair to each fluorine-xenon bond and considers all non-bonding valence electron pairs to be sterically active, is more successful in predicting molecular geometry than the simple m.o. theory, in that it gives the same answers for XeF_2, XeF_4 and $XeOF_4$, but also predicts XeF_6 to be non-octahedral.

Unfortunately the electron-pair-bond description implies the use of outer orbitals, which are energetically far removed[1] from the valence shell. In spite of this, however, and mainly because of the non-octahedral shape of monomolecular XeF_6, the suspicion has lingered on that outer orbitals may be involved by the agency of some ligand field effect.

As far as charge distribution in the xenon fluorides is concerned, n.m.r.[6] and Mössbauer studies[7] have already provided some guidance but since ESCA promised a relatively direct route to the determination of charge distributions and since the method may be applied conveniently to gaseous species as well as condensed phases, we have studied the series of volatile xenon fluorides, XeF_2, XeF_4, XeF_6 and $XeOF_4$. These compounds, furthermore, give a rare opportunity for comparison of volatile compounds of an element in several oxidation states but with common ligand type. In addition, the relationship of xenon oxide tetrafluoride both to xenon tetrafluoride and xenon hexafluoride permits a comparison to be made of the relative electron withdrawing capabilities of oxygen and fluorine in chemical combination with a heavier non-transition element.

THE ESCA METHOD

Since the ESCA method has been described in detail elsewhere[8] only a short summary of the principles will be given here. The compound to be studied is irradiated with X-rays and the expelled electrons are analyzed in a high resolution electron spectrometer. If E_{kin} is the kinetic energy of the expelled photoelectrons and $E_{X\text{-ray}}$ is the quantum energy of the X-radiation, the electron binding energy E_b is obtained from the following relation:

$$E_b = E_{X\text{-ray}} - E_{kin} - C \qquad (1)$$

In studies of solid samples C is equal to the work function of the spectrometer material. The binding energy is then referred to the Fermi level. In measurements on gaseous samples C is a small correction, which is mainly due to contact potential differences. The binding energy for gases is then referred to the vacuum level.

The binding energy for a core shell electron depends on the chemical surroundings of the atom. A "chemical shift" occurs in this binding energy due to change in the effective charge of the atom as a consequence of chemical bonding. In principle then, chemical shifts may be used to derive the charge distribution in different chemical compounds.

Experimental

Preparation and manipulation of samples

The xenon fluorides were prepared by standard procedures. Xenon difluoride was prepared in Pyrex glass[9] and the tetrafluoride[10] and hexafluoride[10] in Monel vessels. The oxide tetrafluoride was made[11] in a Kel-F container by the addition of water to the hexafluoride. All of the compounds were characterized by their gas phase infrared spectra which agreed closely with the spectra reported.[12]

ESCA measurements and results

The study was performed on the 50-cm iron-free double focussing spectrometer at Berkeley. The radiation used to excite the ESCA spectra was $\mathrm{MgK}\alpha_{1,2}$ ($E_{X\text{-}ray} = 1253.6$ eV) and the detector was an electron channel multiplier.

The samples, Xe, XeF_2, XeF_4, XeF_6 and $XeOF_4$, were studied in the gaseous as well as in the solid phase. The compounds were stored in bottles outside the spectrometer and provision was made for a continuous flow of gas into a small source chamber situated near the X-ray anode and separated from the X-ray compartment by a thin beryllium window. When the compounds were studied in the solid phase a plate cooled by liquid nitrogen was introduced in the chamber and the gas became continuously solidified on its surface. The expelled electrons were in both types of study allowed to enter the spectrometer through a narrow slit (width varied between 0.2 and 0.5 mm). This slit served two purposes: it defined a narrow electron source for the spectrometer, and it made provision for a differential pumping of the gas in order to maintain a much higher pressure in the source chamber than in the X-ray compartment and the spectrometer vacuum chamber. A fairly good intensity at a high resolution was thereby obtained for the recorded spectra. Usually two or more gases were let into the chamber simultaneously, thus making it possible to achieve a direct measurement of the shifts. For calibration, the binding energies for gaseous xenon, as determined at Uppsala,[13] were used.

The first set of measurements was performed on the compounds in the solid phase. For all the abovementioned compounds the ESCA spectra of the M_{IV}, M_V, N_{III} and $N_{IV,V}$ levels in xenon and the K level in fluorine were recorded. Examples of the spectra are shown in Figs. 1 and 2. For each compound the chemical shifts were found to be the same for all levels in xenon (within an experimental accuracy of a few tenths of an eV). Due to this agreement the main measurements on the compounds in the gaseous phase were performed only on one level. The level XeM_V was chosen since the corresponding ESCA line (compare Fig. 1) is strong and does not coincide with ESCA spectra of other levels.

For the measurements on the compounds in the gaseous phase, xenon and one or two of the xenon compounds were let into the chamber simultaneously. The ESCA spectrum of the XeM_V level was recorded at least three times for each mixture. Examples of the spectra are given in Figs. 3-6 and the mean values of the shifts obtained are given in Table 1. The limits of error corresponds to two standard deviations. For the fluorides the shift in the level energy is given, in Fig. 7, as a function of oxidation number. The correlation curve is very smooth.

Discussion

The xenon core electrons, in the xenon fluorides, typified by XeM_V, become increasingly more bound as the ligand number increases, therefore the xenon valence shell must lose electron density to the ligands. The energy change per ligand decreases in proceeding from XeF_2 to XeF_6 (see Table 1) and this fits the expectation that electron removal should become more difficult as the positive charge on the xenon is increased.

To assess the charge distribution the simplest ionic model is convenient. In this device the xenon valence shell loses charge -q but retains its spherical symmetry. Each ligand atom acquires an appropriate negative charge, q_F, which is considered to have its effective center at the ligand nucleus. Xenon difluoride is therefore visualized as $F^{q/2^-}Xe^{q^+}F^{q/2^-}$. If, for the general case, we let the xenon valence shell radius be $r_v(Xe)$, the internuclear Xe-F distance be R and the xenon valence shell is treated as a spherical conductor, then

$$\Delta E = q\left(\frac{1}{r_v(Xe)} - \frac{1}{R}\right), \qquad (2)$$

with which, for all quantities in atomic units, q is given as the number of electrons transferred from the xenon atom to the fluorine ligands. This equation contains two unknowns, q and $r_v(Xe)$.

The dependence of the negative charge on each fluorine ligand, q_F, in each of the three binary xenon fluorides, upon the choice for the xenon valence shell radius, $r_v(Xe)$ is shown in Table 2 and Fig. 8. It is remarkable that for all three binary fluorides, the q_F versus $r_v(Xe)$ curve is, within the experimental error, the same. It is evident that a significant part of the decrease in ΔE per F ligand, with increase in oxidation number of the xenon atom, is due to the associated decrease in R. The values previously assigned to R are included in Table 1. Note that if r_v(Xe) did not change with change in charge, q_F would be constant in the series of xenon fluorides and the charge developed on the central xenon atom would be directly proportional to the number of fluorine ligands.

In order to obtain a measure of r_v(Xe) the mean value of the radius of the valence shell ($5p_{3/2}$) was calculated using a program developed by A. Rosén and I. Lindgren[14] for calculation of electron binding energies.* In this program relativistic wave functions and a modified Hartree-Fock-Slater method were used. The $5p_{3/2}$ electrons were removed one by one and the valence shell radius was calculated. In Fig. 8 is shown the dependence of the Xe, $5p_{3/2}$ shell radius upon the charge q_F, on each fluorine atom, for each fluoride. The crossing points of these curves and the curve representing

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*The authors are greatly indebted to fil. lic. Arne Rosén who performed the calculations.

the dependence of q_F upon $r_v(Xe)$, obtained from the ESCA measurements, indicate q_F and $r_v(Xe)$ in each compound. The numerical values are given in Table 3. Because our model is oversimplified these values must be somewhat approximative.**

** An alternative estimate, of each valence shell radius may be made, if we assume our 'device' to be close to reality. Since $r_v(Xe)$, for our spherical cation model, must decrease from Xe(II) to Xe(IV) to Xe(VI), it is clear, from Figure 8, that q_F must also decrease similarly. But the internuclear distance, R, decreases by 0.05 Å from XeF_2 to XeF_4 and from XeF_4 to XeF_6. We can take this to represent mainly a decrease in $r_v(Xe)$, since, from Figure 8, for changes of 0.05 Å, the change in charge on the fluorine ligands is never more than 0.07<u>e</u> for all reasonable values of $r_v(Xe)$. Furthermore the greater ligand-ligand repulsions in the higher fluorides could offset any decrease in the F ligand size and even allow $r_v(Xe)$ to decrease by > 0.05 Å for each increase of two units in oxidation number. It is a reasonable assumption, however, that the bond shrinkage represents $r_v(Xe)$ shrinkage.

Furthermore if we assume that the valence shell radius is determined primarily by electron repulsion and that

$$\frac{8 - q}{4\pi(r_v(Xe))^2} = \text{constant, then}$$

$$r_v(XeF_4) = r_v(XeF_2) \times \sqrt{\frac{8 - q_{Xe}(XeF_4)}{8 - q_{Xe}(XeF_2)}}$$

For a given choice of $r_v(XeF_2)$ and its related $q_{Xe}(XeF_2)$, $r_v(XeF_4)$ may be obtained iteratively by applying an approximate choice of $q_{Xe}(XeF_4)$ to obtain an approximate $r_v(XeF_4)$ which, in turn, is used to obtain a more reliable value for $q_{xe}(XeF_4)$ from the relationship (2), until self consistent results are obtained. With this relationship a choice of $r_v(XeF_2)$ of 1.4 Å gives $r_v(XeF_4)$ = 1.33 Å, i.e. $r_v(XeF_2) - r_v(XeF_4)$ = 0.07 Å, which seems too large a change, but for $r_v(XeF_2)$ = 1.3 Å, $r_v(XeF_4)$ = 1.25 Å and for $r_v(XeF_2)$ = 1.2 Å, $r_v(XeF_4)$ = 1.155 Å. Therefore applying the criterion that the valence shell electron density per unit area is constant and that the change in valence shell radius $r_v(XeF_2) - r_v(XeF_4)$ be 0.05 Å, the best choice of $r_v(XeF_2)$ lies between 1.2 and 1.4 Å. From this procedure $r_v(XeF_2)$

In particular, polarization of the anions by the cations should result in a shift of the negative charge center towards the cation. This implies that we have overvalued R and hence undervalued q_F. The q_F values could, therefore, be ~ 0.5 e, which is the charge transfer predicted[1] by the simplest three center m.o. treatments.

Furthermore, Koopmans' approximation /15/ has been assumed to be valid, i.e. valence electron relaxation has been neglected. Although the core binding energies are lower than those calculated /8/ using Koopmans' approximation (for XeM_V for instance 676.3 eV /13/ compared to 693 eV /8/) the influence on the shifts can generally be assumed to be small /8/. With a couple of exceptions satisfactory agreement between experimental results and calculations of binding energy shifts using Koopmans' approximation

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is ~ 1.3 Å, $q_F(XeF_2) = 0.38$; $r_v(XeF_4) = 1.25$ Å, $q_F(XeF_4) = 0.33$, $r_v(XeF_6) = 1.20$ Å and $q_F(XeF_6) = 0.30$. Thus the positive charge on the xenon atom in the three fluorides would be: XeF_2, 0.76; XeF_4, 1.32 and XeF_6, 1.80. This represents fair agreement with the results given in Table 3.

are reported in refs. 13 and 16.

The case of xenon oxide tetrafluoride gives further support for the molecular orbital approach. The structural parameters obtained by Martins and Bright Wilson[17] for $XeOF_4$: Xe-F, 1.95 ± 0.05 Å; Xe-O, 1.70 ± 0.05 Å; F-Xe-O, 91 ± 2° show that the XeF_4 part of the molecule is (within the quoted errors) indistinguishable from the XeF_4, (Xe-F, 1.95 ± 0.01 Å) molecule. Indeed the $XeOF_4$ molecule looks remarkably like an unperturbed XeF_4 molecule bearing an oxygen atom on its fourfold axis. Now for $XeOF_4$:

$$\Delta E(XeOF_4) = \frac{4q_F(XeOF_4) + q_O}{r_v(XeOF_4)} - \frac{4q_F(XeOF_4)}{R(Xe-F)} - \frac{q_O}{R(Xe-O)}$$

$$= \frac{4q_F(XeOF_4)}{r_v(XeOF_4)} - \frac{4q_F(XeOF_4)}{R(Xe-F)} + \frac{q_O}{r_v(XeOF_4)} - \frac{q_O}{R(Xe-O)}$$

If we allow that $q_F(XeOF_4) = q_F(XeF_4)$ and that $r_v(XeOF_4) = r_v(XeF_4)$, since R(Xe-F) is the same in both molecules (1.95 Å), then

$$\Delta E(XeOF_4) = \Delta E(XeF_4) + q_O \left(\frac{1}{r_v(XeOF_4)} - \frac{1}{R(Xe-O)} \right).$$

Since all but $r_v(XeOF_4)$ and q_O are known, the dependence of the valence shell radius upon the oxygen charge can therefore be evaluated and is represented in Table 4. Of course it is probable that our assumptions have overvalued q_F and overvalued $r_v(XeOF_4)$ but to some extent these overevaluations will cancel. However we can obtain the q_O dependence upon $r_v(XeOF_4)$ in a different way. If we let $q_F(XeOF_4) = q_F(XeF_6)$ and $r_v(XeOF_4) = r_v(XeF_6)$ then we can write

$$\Delta E(XeOF_4) = \frac{2}{3} \Delta E(XeF_6) + q_O' \left(\frac{1}{r_v(XeOF_4)} - \frac{1}{R(Xe-O)} \right)$$

and again are able to determine the dependence of the oxygen ligand charge (q_O') upon $r_v(XeOF_4)$. This dependence is also shown in Table 4 and the results are seen to be very similar to those from the other approximation. The last approximation should underestimate both q_F and $r_v(XeOF_4)$. We would therefore expect the mean of the two results for the oxygen charge $(\frac{q_O' + q_O}{2})$ to represent the true situation better than either approximation. In any case the difference between q_O' and q_O is not considered to be significant for our purposes.

As the results in Table 4 and the curves in Fig. 9 show, the electron withdrawal by the oxygen ligand is considerably greater than the withdrawal by each of the fluorine ligands. The relative electron withdrawing capacity depends upon the choice of $r_v(XeOF_4)$. If the mean of the calculated $r_v(XeF_4)$ and $r_v(XeF_6)$ is used, $q_O = 0.44$ and $q_F = 0.28$. On the other hand, if $r_v(XeOF_4)$ is taken to be 1.25 Å (see footnote p 12 ms), $q_O = -0.54$ and $q_F = -0.33$. Note, that for q_F to be $=$ 0.5, as predicted by the simplest three center, four electron m.o. approach,[2a], $r_v(XeOF_4)$ is required to be = 1.42 Å, but the charge on the oxygen ligand (q_O = 0.99) approaches unity. As has already been pointed out above, the polarization of the ligand charge by the central atom probably causes R to be overvalued. A greater value for r_v(Xe) would compensate for this error. Therefore the value of $r_v(XeOF_4)$ = 1.42 Å may not be unrealistic. Of course if higher orbitals (4_f_ or 5_d_) are not used, it is convenient to assume that the oxygen ligand is bonded to the xenon atom by the agency of a semi-ionic linkage $F_4Xe^+{:}O^-$. This, plus two 3 center 4 electron m.o. bonds for the fluorine ligands, yields the charge distribution $(F^{\frac{1}{2}-})_4Xe^{3+}O^{1-}$ for the molecule.

Since the charge on the oxygen ligand probably exceeds 0.4 ($r_v(XeOF_4)$ = 1.15 Å) in $XeOF_4$ and since the XeF_4 part, within the experimental error, is planar, the molecule should have a dipole moment $\mu > 4D$, if the non-bonding valence electron pair is 5_s_. If the moment should prove to be low, we can be confident of the non-bonding pair being in an _sp_ hybrid orbital.

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Table 1. Chemical shifts in the XeM_V level for some xenon compounds studied in the gaseous phase. The internuclear Xe-F distances R are also given.

Compound	Shift ΔE (eV)	Shift per fluorine atom (eV)	R (Å)	ref.
Xe	0			
XeF_2	2.95 ± 0.13	1.48	2.00 ± 0.01	18
XeF_4	5.47 ± 0.18	1.37	1.95 ± 0.01	19
$XeOF_4$	7.02 ± 0.13		1.95 ± 0.05	17
XeF_6	7.88 ± 0.18	1.31	1.89 ± 0.005	4

Table 2. Dependence of charge distribution upon choice of valence shell radius (r_v) of the xenon atom in XeF_2, XeF_4 and XeF_6.

r_v(Å)	1.5	1.4	1.3	1.2	1.1	1.0	0.9	0.8
$q_F(XeF_2)$	0.61	0.48	0.38	0.31	0.25	0.20	0.17	0.14
$q_F(XeF_4)$	0.62	0.47	0.37	0.30	0.24	0.19	0.16	0.13
$q_F(XeF_6)$	0.66	0.50	0.38	0.30	0.24	0.19	0.16	0.13

q_F is the net negative charge on each F ligand.

Table 3. Valence shell radius r_v for Xe and charges obtained for the Xe atom and the ligands in the compounds studied, using theoretically derived r_v values.

Compound	r_v(Å)	q_{Xe}	q_F	q_O
XeF_2	1.22	0.62	0.31	
XeF_4	1.19	1.16	0.29	
XeF_6	1.16	1.62	0.27	
$XeOF_4$	1.18	1.56	0.28	0.44

Table 4. Charge distribution in $XeOF_4$ as a function of the valence shell radius r_v.

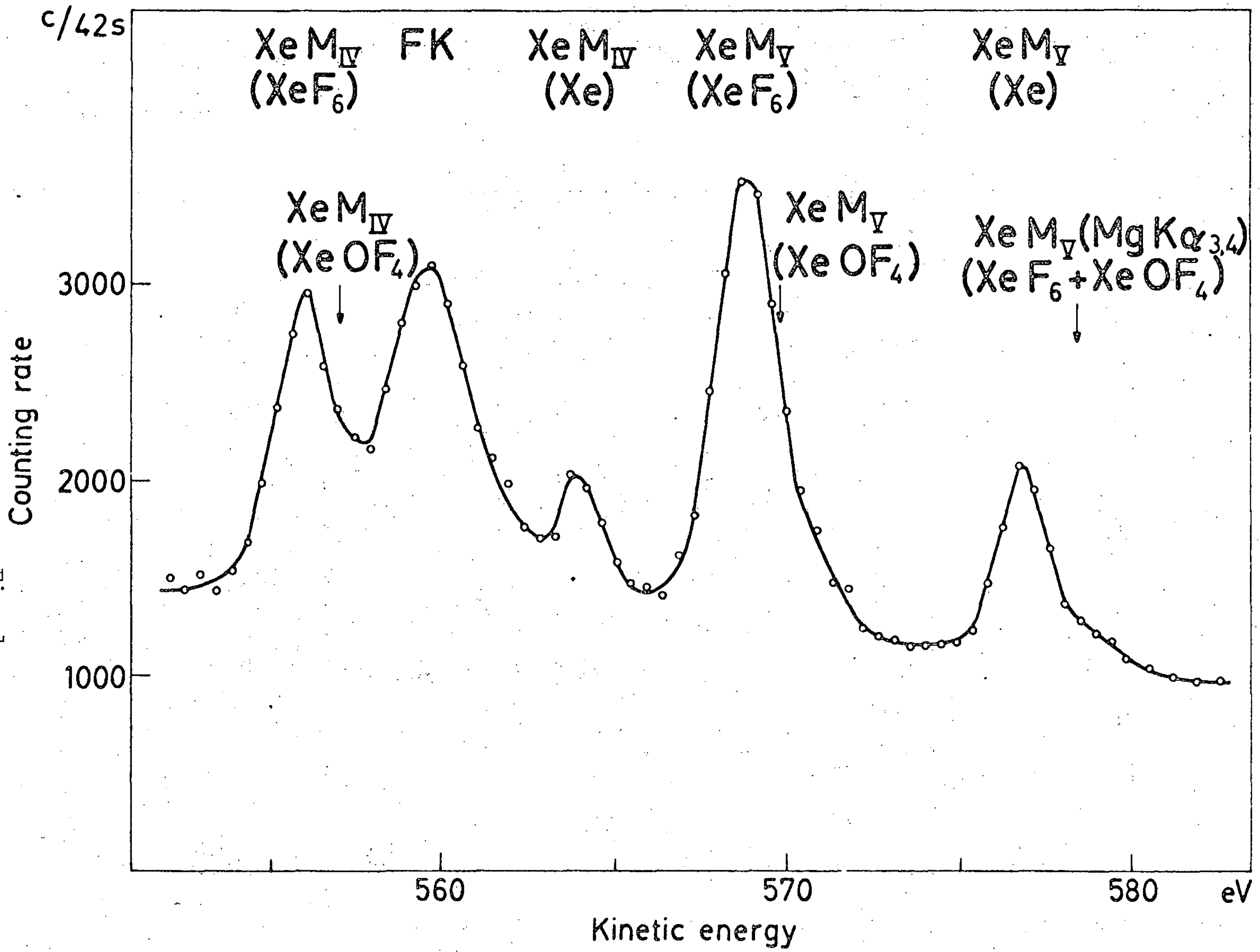
r_v(Å)	1.5	1.4	1.3	1.2	1.1	1.0	0.9	0.8
q_o'	1.6	0.98	0.68	0.50	0.38	0.30	0.24	0.19
q_o	1.4	0.85	0.59	0.44	0.34	0.26	0.21	0.16
$\frac{q_o'+q_o}{2}$	1.5	0.91	0.64	0.47	0.36	0.28	0.22	0.17
q_F	0.63	0.48	0.37	0.30	0.24	0.20	0.16	0.13

q_o' is the charge on the oxygen ligand assuming $r_v = r_v(XeF_6)$ and interatomic distance Xe-F = 1.89 Å (ref. 4).

q_o is the charge on the oxygen ligand assuming $r_v = r_v(XeF_4)$ and interatomic distance Xe-F = 1.95 Å (ref. 17).

measurements (ESCA) and according to the calculation for XeF_2, XeF_4 and XeF_6.

Fig. 9. A comparison of electron withdrawal by oxygen and fluorine ligands in $XeOF_4$.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Xe M_{IV} (XeF_6)
FK
Xe M_{IV} (Xe)
Xe M_{V} (XeF_6)
Xe M_{V} (Xe)
Xe M_{IV} ($XeOF_4$)
Xe M_{V} ($XeOF_4$)
Xe M_{V} (Mg K$\alpha_{3,4}$) (XeF_6 + $XeOF_4$)
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2000
1000
Counting rate
560
570
580
eV
Kinetic energy

Fig. 1

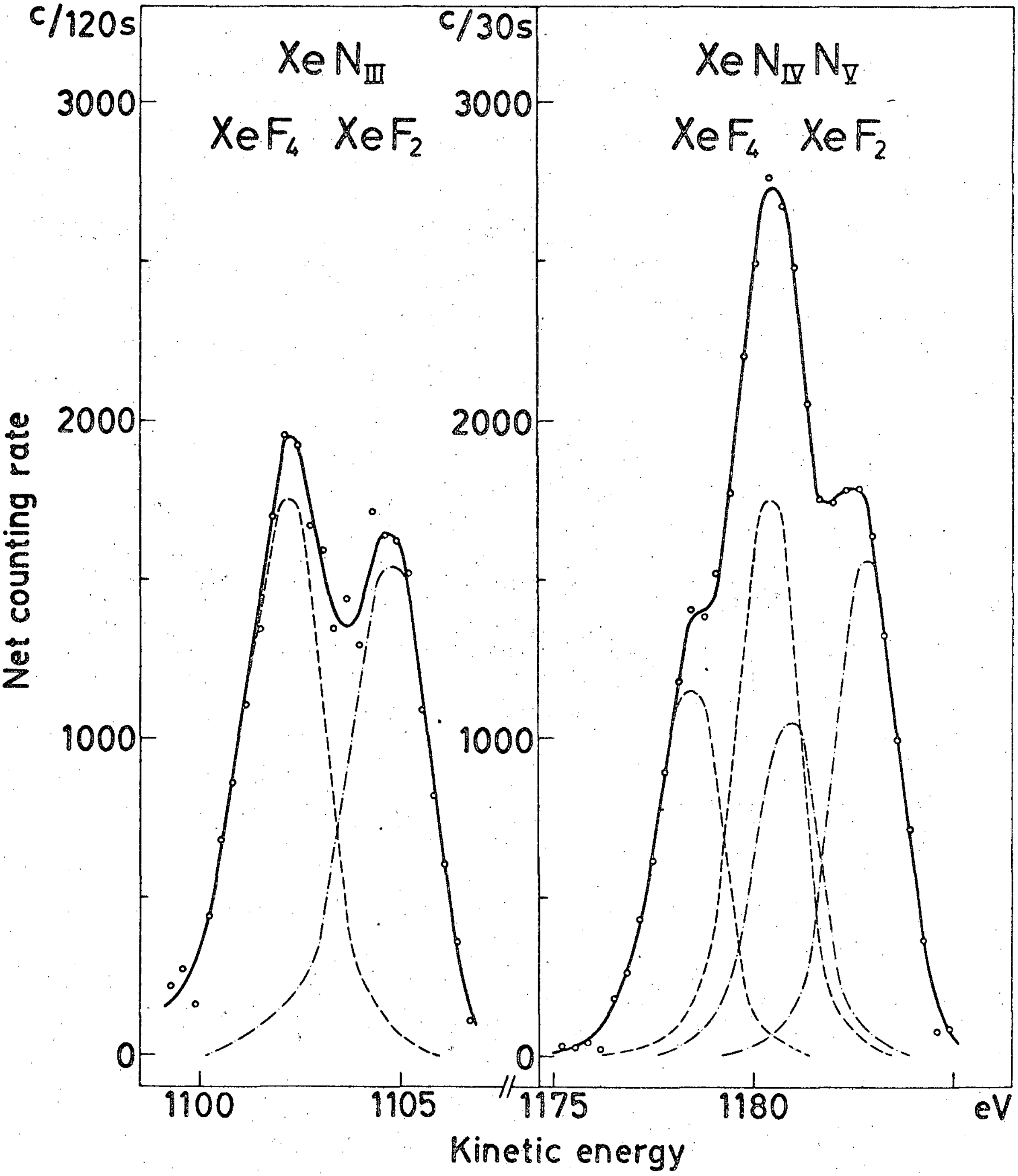
c/120s
Xe N$_{III}$
XeF$_4$ XeF$_2$
3000
2000
1000
0
c/30s
Xe N$_{IV}$ N$_{V}$
XeF$_4$ XeF$_2$
3000
2000
1000
0
Net counting rate
1100
1105
1175
1180
eV
Kinetic energy

Fig. 2

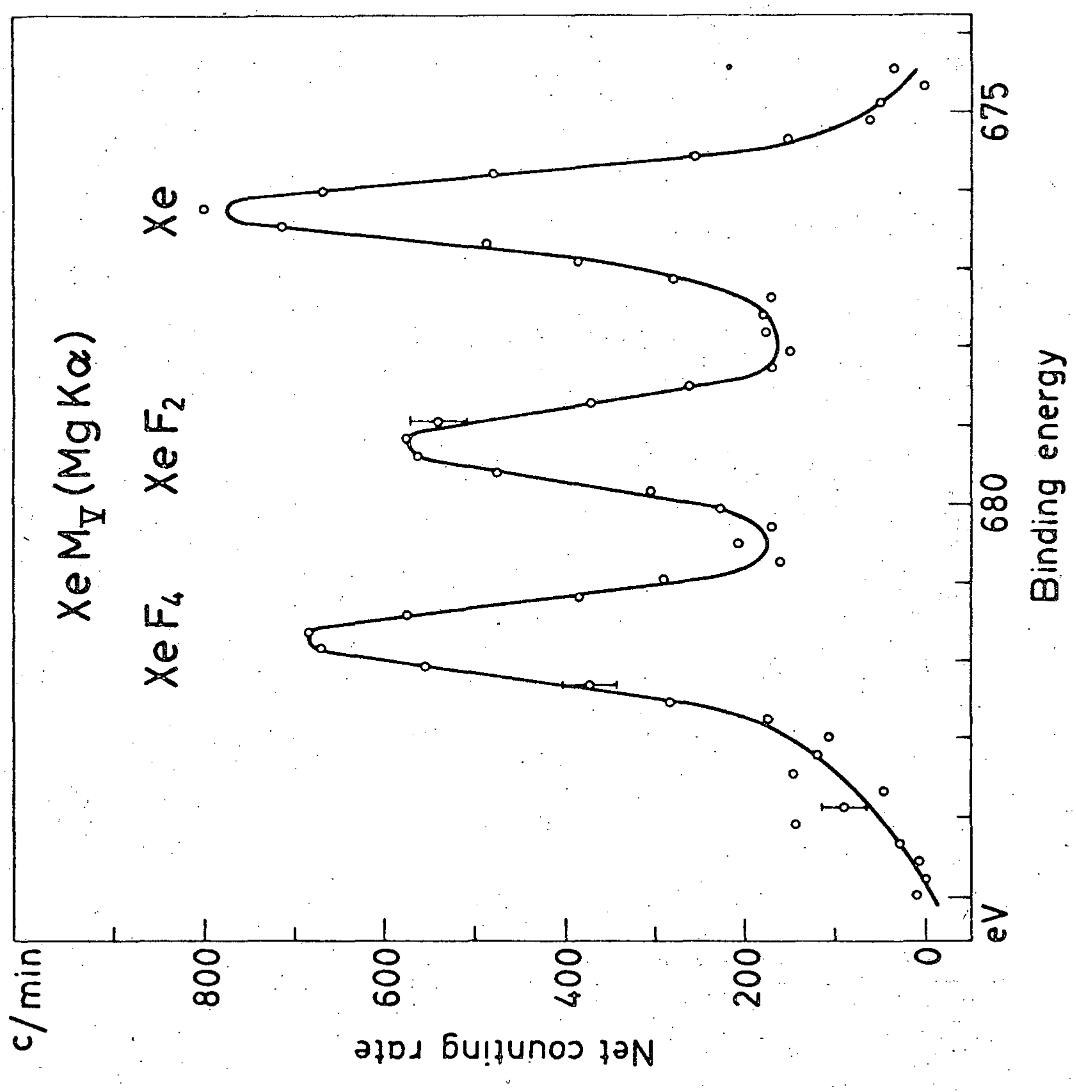
Xe M_{V} (Mg Kα)
Xe F_4
Xe F_2
Xe
c/min
Net counting rate
800
600
400
200
0
eV
680
675
Binding energy

Fig. 3

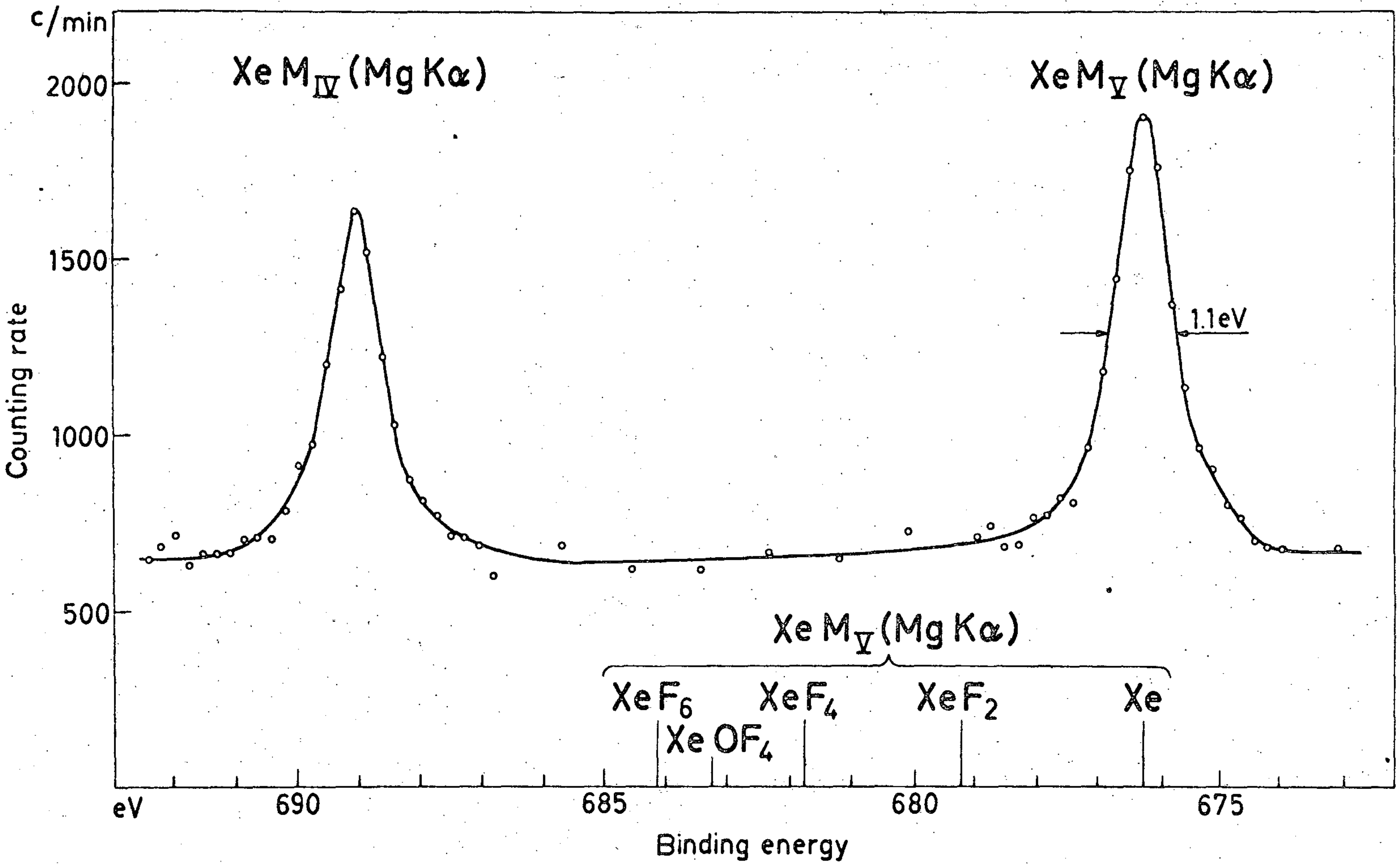
c/min
Counting rate
2000
1500
1000
500
Xe M_{IV} (Mg Kα)
Xe M_{V} (Mg Kα)
1.1eV
Xe M_{V} (Mg Kα)
XeF_6
XeOF_4
XeF_4
XeF_2
Xe
eV
690
685
680
675
Binding energy

Fig. 4

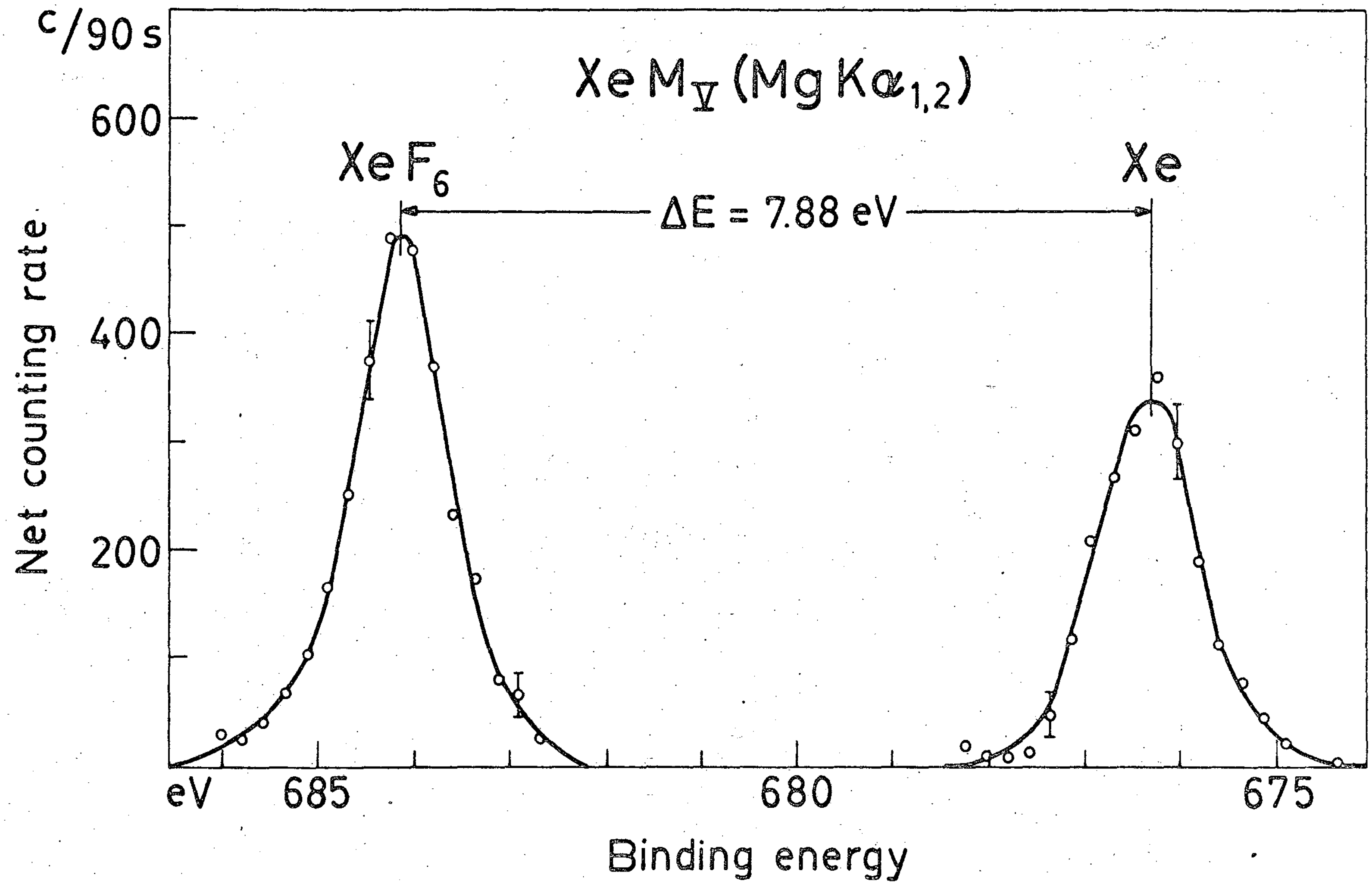
c/90 s
Xe M_V (Mg Kα_{1,2})
600
400
200
Net counting rate
XeF_6
Xe
ΔE = 7.88 eV
eV
685
680
675
Binding energy

Fig. 5

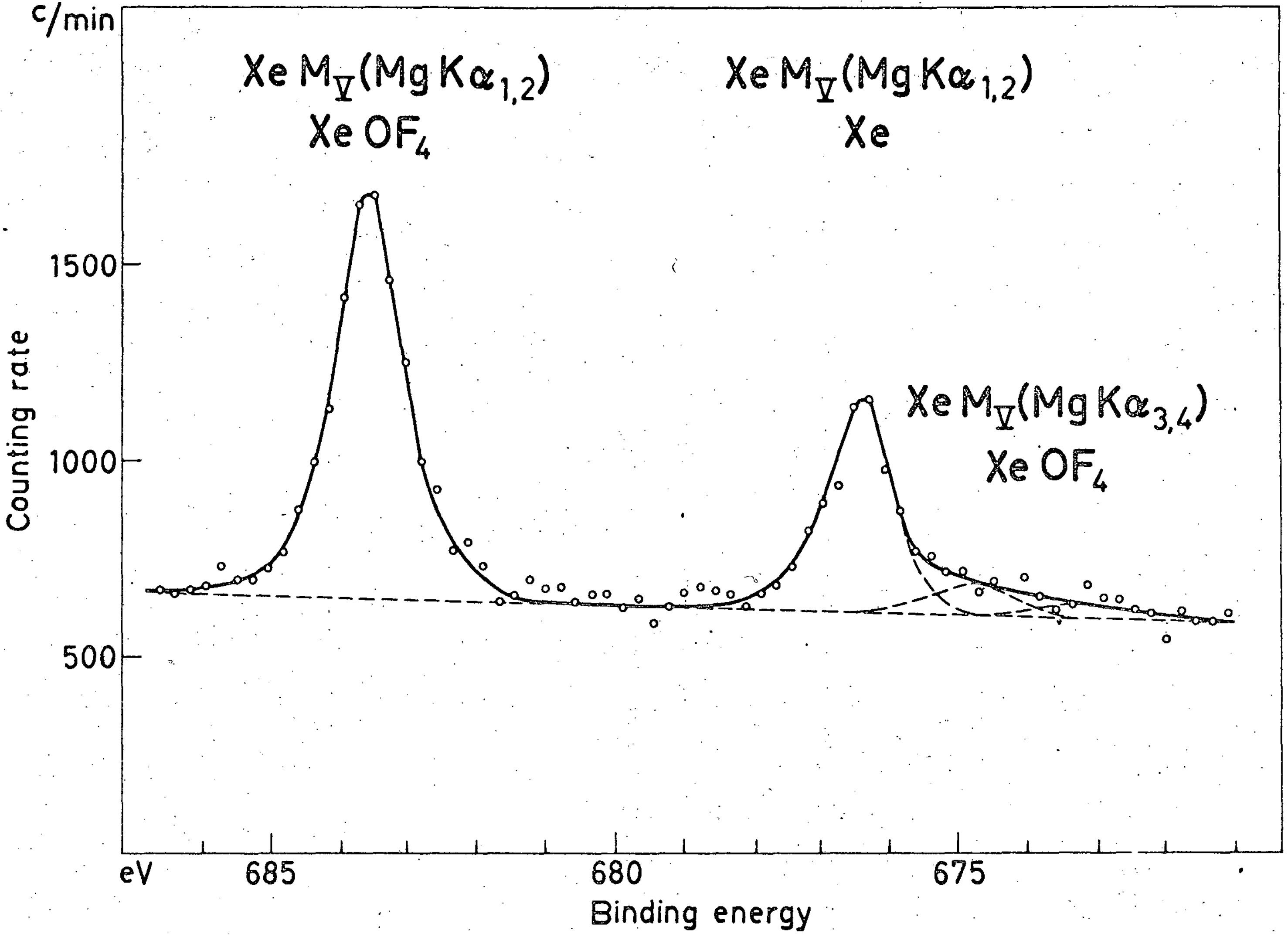
c/min
Xe M_V(Mg $K\alpha_{1,2}$)
Xe OF_4
Xe M_V(Mg $K\alpha_{1,2}$)
Xe
Xe M_V(Mg $K\alpha_{3,4}$)
Xe OF_4
1500
1000
500
Counting rate
eV
685
680
675
Binding energy

Fig. 6

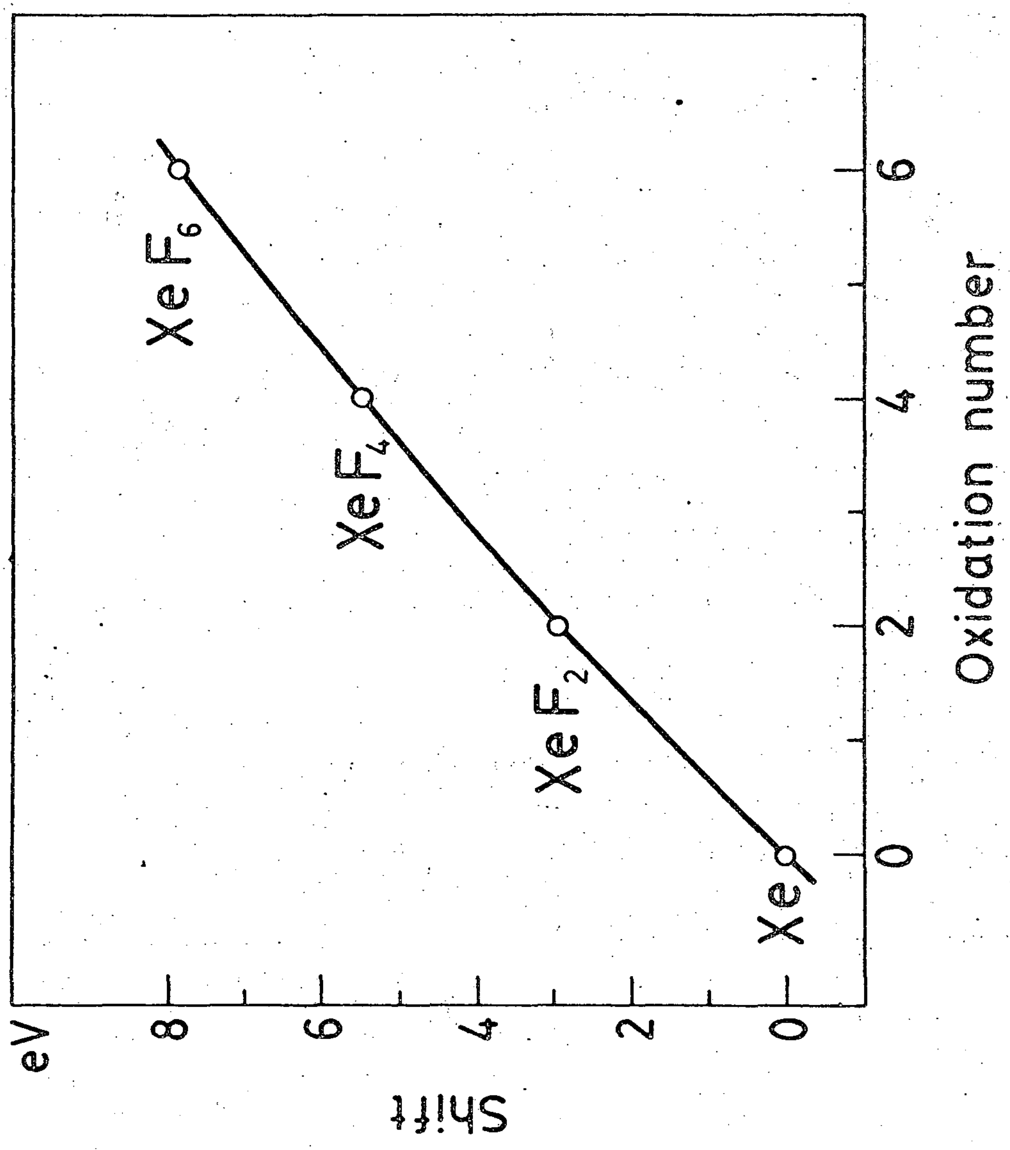

Fig. 7

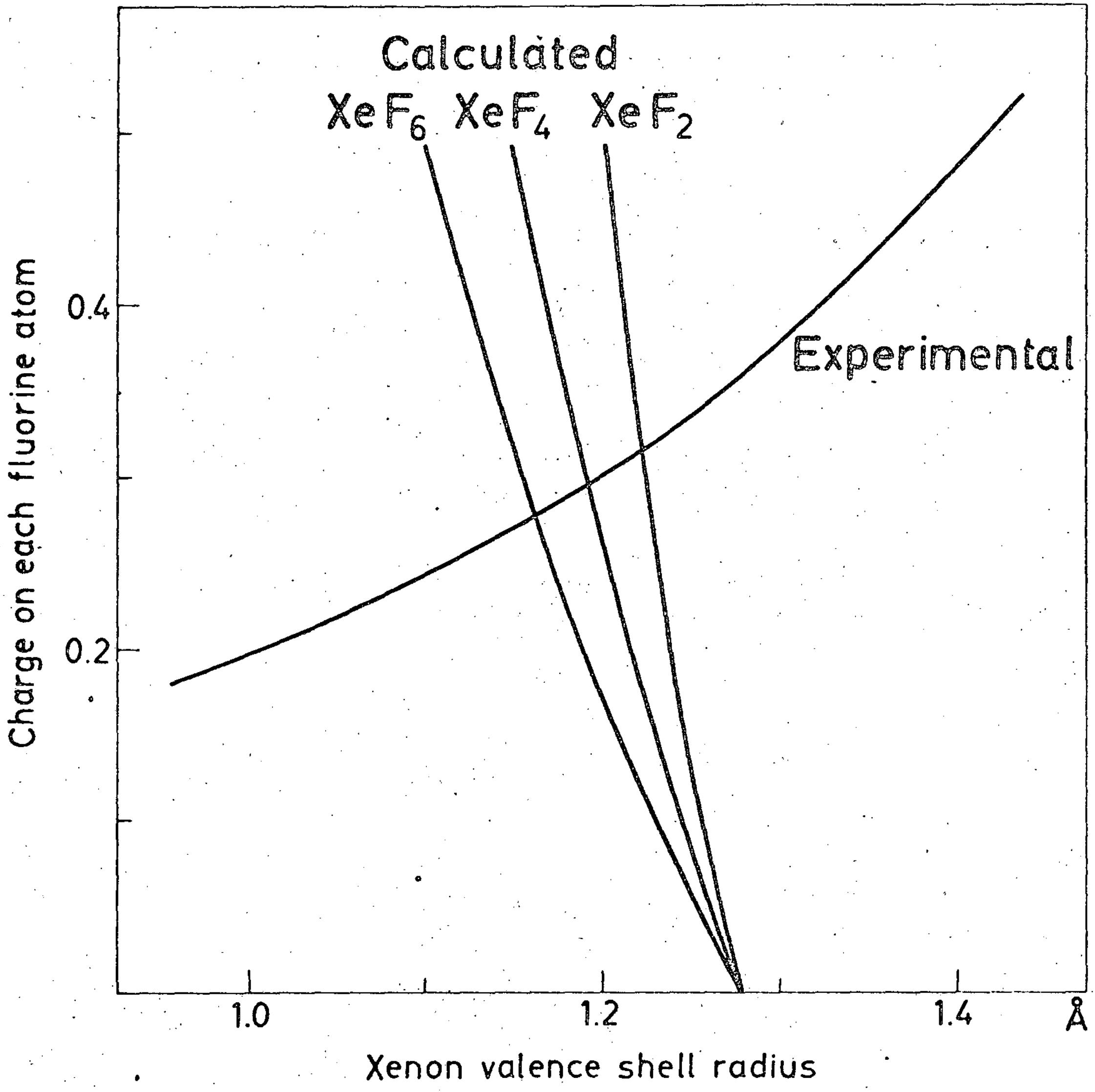
Calculated
XeF_6
XeF_4
XeF_2
Experimental
Charge on each fluorine atom
0.4
0.2
1.0
1.2
1.4
Å
Xenon valence shell radius

Fig. 8

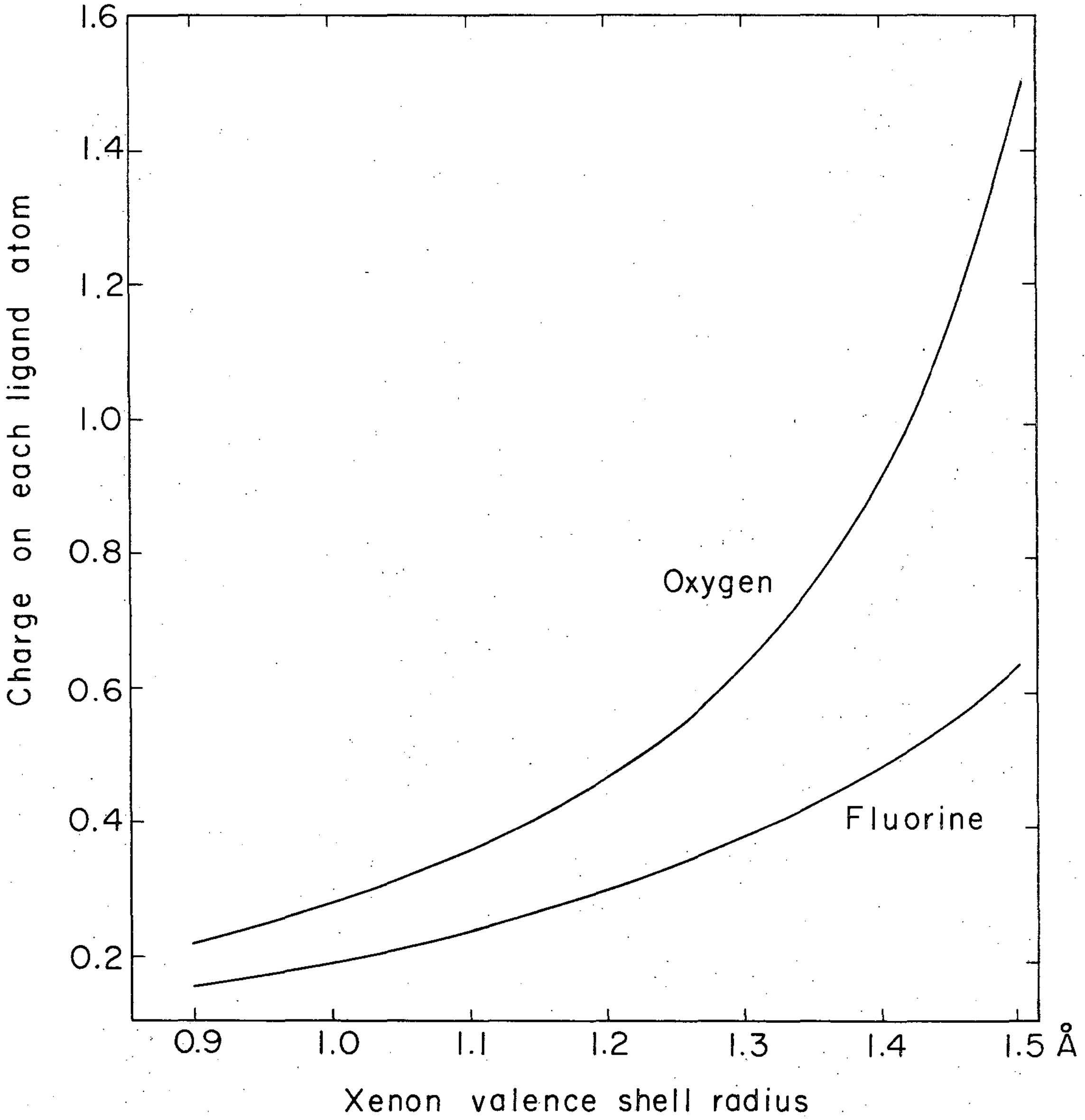

Fig. 9

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